INVESTIGATOR'S ANNUAL REPORT

United States Department of the Interior

National Park Service

All or some of the information you provide may become available to the public.

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Reporting Year:	**Park:**	**Select the type of permit this report addresses:**
2009	Shenandoah NP	Scientific Study

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Project Title (maximum 300 characters):

Linked Hydrologic and Atmospheric Mercury Fluxes in a High-Elevation Wetland

Park-assigned Study or Activity #:	**Park-assigned Permit #:**	**Permit Start Date:**	**Permit Expiration Date:**
SHEN-00340	SHEN-2007-SCI-0010	Jun 20, 2007	Mar 31, 2012

Scientific Study Starting Date:	**Estimated Scientific Study Ending Date:**
Jun 20, 2007	Mar 31, 2012

For either a Scientific Study or a Science Education Activity, the status is:

Continuing

For a Scientific Study that is completed, please check each of the following that applies:

__ A final report has been provided to the park or will be provided to the park within the next two years

__ Copies of field notes, data files, photos, or other study records, as agreed, have been provided to the park

__ All collected and retained specimens have been cataloged into the NPS catalog system and NPS has processed loan agreements as needed

Activity Type:

Research

Subject/Discipline:

Wetlands / Floodplains

Purpose of Scientific Study or Science Education Activity during the reporting year (maximum 4000 characters):

The accumulation of mercury (Hg) in the environment from atmospheric deposition is a worldwide problem that has gained attention relatively recently [Krabbenhoft, 2004]. The form of mercury that is particularly toxic is methylmercury (MeHg), which is formed by the bacterial transformation of ionic mercury (Hg2+) and efficiently bioaccumulates in the food chain. It is estimated that

approximately 630,000 children born each year in the U.S. alone are exposed to elevated methylmercury levels in the womb, putting them at risk of impaired neurological development [Mahaffey, 2004]. Only now are we beginning to fully grasp the widespread impact that this problem is having on human health, affecting localities hundreds of miles away from emission sources [Driscoll et al., in press]. Mercury concentrations in the atmosphere have increased 2-5 times those of pre-industrial levels [EPA, 1997] leading to increased deposition. However, it is the transformation processes that occur upon deposition within watersheds that ultimately affect the bioavailability of this toxin. Although the impact of the mercury problem is wide-ranging, the specific processes that control mercury cycling in the environment remain poorly understood.

Statistical relationships between watershed physical descriptors and mercury concentrations are relatively weak, but two key controls are worth noting. First, the degree of watershed forestation is positively related to Hg concentration since trees scavenge Hg vapor through stomatal uptake [Ericksen et al., 2003] and because organic matter is typically abundant in forested systems. Second, watersheds with wetlands tend to have high concentrations of MeHg, since reducing conditions are more favorable in these areas [Grigal, 2002]. Overall, controls on mercury concentrations are quite complex, and high spatial variability can be found within limited geographical areas. For example, preliminary measurements taken in Shenandoah National Park (SNP), Virginia at 15 sites found HgT concentrations to be fairly low, ranging from 0.104 ng/L to 0.651 ng/L. Deviations from these low levels were discovered in the Big Meadows area of SNP, an extensive wetland area that is the location of the proposed research. Here, total mercury concentrations in surface water were much higher, ranging from 1.77 ng/L to 4.66 ng/L [C. Moore., pers. comm.]. These concentrations are consistent with a setting in which bioaccumulation of mercury is a general problem. Streams that drain this wetland area, however, have reduced total mercury concentrations, raising the question of which transformations and fluxes are responsible for dramatically altering the stream mercury concentrations along the hydrological flowpaths within the wetland.

We would like to develop a processed-based understanding of how mercury is transformed in natural environments by simultaneously measuring both aqueous and atmospheric fluxes. The large gradient in mercury levels over short distances in the Big Meadows area of SNP provides us with an ideal natural laboratory to understand how mercury moves through the natural environment. The ultimate goal is to scale up this information to predict other areas within SNP that are vulnerable to elevated stream water levels of mercury and mercury bioaccumulation.

Findings and status of Scientific Study or accomplishments of Science Education Activity during the reporting year (maximum 4000 characters):

Atmospheric Studies:

Seasonal patterns of atmospheric mercury (Hg) fluxes measured over vegetated terrestrial systems can provide insight into the underlying process controlling emission and deposition of Hg to vegetated surfaces. Gaseous elemental Hg fluxes were measured for week-long periods in each season (spring, summer, fall, and winter) over an uncontaminated high-elevation wetland meadow (Big Meadows) in Shenandoah National Park, Virginia using micrometeorological methods. Mean net deposition was observed in the spring (â 4.8 ng mâ 2 hâ 1), emission in the summer (2.5 ng mâ 2 hâ 1), near zero flux in the fall (0.3 ng mâ 2 hâ 1), and emission in the winter (4.1 ng mâ 2 hâ 1). Nighttime deposition (when stomata are closed) and the poor correlation between Hg fluxes and canopy conductance during periods of active vegetation growth suggest that stomatal processes are not the dominant mechanism for ecosystem-level GEM exchange at this site. The strong springtime deposition relative to summer implies that young vegetation is better at scavenging Hg, with the highest deposition occurring at night possibly via a cuticular pathway. These results suggest that spring is a period of GEM deposition while other seasons exhibit net emission, emphasizing the importance of capturing GEM flux seasonality when determining total Hg budgets.

In 2008-09, we measured Hg concentrations in dew using traditional physical sampling techniques and modeled dew depth over natural surfaces using a micrometeorological approach. A surface energy budget model adequately predicted dew deposition. Concentrations of Hg in dew (mean: 5.57 ng L-1) were similar to those seen in rainfall, but the estimated yearly dew depth (~20 mm) was considerably less than the rainfall depth measured in 2008 (~1400 mm). Frost samples had significantly higher Hg concentrations than liquid dew samples, but there was not significant difference in mass of Hg deposited. Cumulative nighttime GEM fluxes on nights prior to dew formation were not correlated with Hg concentrations in dew. In addition, the diel patterns in GEM fluxes did not track dew formation (i.e. no GEM deposition signal at the onset of dew formation and no GEM emission pulse when dew evaporated). On a seasonal or yearly scale, the Hg deposition in rainfall and deposition/emission to the atmosphere are 2-3 orders of magnitude greater than Hg deposited into dewfall. Additional work is needed to determine if the Hg deposited in dew remains on the surface, or if it is released back to the atmosphere.

Stream studies:

Headwater terrestrial systems are a primary source of downstream contamination because they store large pools of mercury (Hg) in

soils and sediments. We are currently evaluating Hg dynamics in three forested headwater catchments (Paine Run, Staunton River, and Piney River) in SHEN. The remote catchments are located within 100 kilometers of one another, have similar physical features (size, slope, and vegetation) but are distinct in chemical and hydrological characteristics. Starting in March 2009, we have been measuring dissolved and particle-bound Hg, DOC, UV-absorbance at 254 nm, pH, and discharge within the three catchments on a bi-weekly basis. During storm events, samples are taken at 2-hr increments with automated Iscoâ s retrofitted for Hg sampling. For each site we quantify fluxes of particulate and dissolved Hg and determine how/if the relationship between DOC and dissolved Hg varies during storm events. We also examine how DOC quality affects Hg transport. Ultimately, this analysis will offer insight into how the hydrology and water chemistry of a catchment affect the timing, amount, and physical fractioning of Hg transport, specifically during storm events.

For Scientific Studies (not Science Education Activities), were any specimens collected and removed from the park but not destroyed during analysis?

No

Funding specifically used in this park this reporting year that was provided by NPS (enter dollar amount):	**Funding specifically used in this park this reporting year that was provided by all other sources (enter dollar amount):**
$0	$40000

List any other U.S. Government Agencies supporting this study or activity and the funding each provided this reporting year: